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BUBLEWITZ ET AL-14 PCT

In re Application of: Alexander BUBLEWITZ ET AL

Application No.: 10/589,329

Filed: AUGUST 14, 2006

For: DENTAL MATERIAL BASED ON ALKOXYSILYL-FUNCTIONAL POLYETHERS CONTAINING A SALT OF A STRONG BASE AS CATALYST

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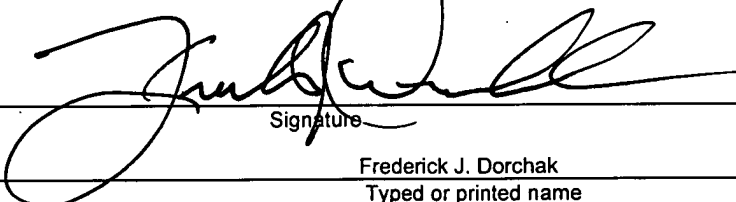
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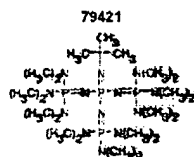
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 Introduction / Monomeric Phosphazene Bases (P1)  
 Dimeric Phosphazene Bases (P2) / Tetrameric Phosphazene Bases (P4)
**Tetrameric Phosphazene Bases (P4)**

The two P<sub>4</sub> phosphazene bases offered by Fluka differ slightly with respect to their steric hindrance and basicity (Table 5).

**Table 5. Order of Basicity for P<sub>4</sub> Bases**

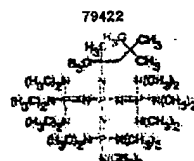
Order of steric hindrance:	P4-t-Oct	>>	P4-t-Bu
Fluka Product Number:	78422		79421
Basicity ( <sup>MeCN</sup> pK <sub>BH+</sub> ):	42.7		41.9

P4-t-Bu<sup>[1]</sup> 79421 and P4-t-Oct 78422, offered as 1 M solutions in hexane have several important features. They are highly sterically hindered, extremely hygroscopic, highly stable towards hydrolysis, 18 orders of magnitude more basic than DBU,<sup>[2]</sup> and already in the basicity range typical of organolithium bases. Both 79421 and 78422 are particularly suitable for deprotonation (activation) of pronucleophiles, although also deprotonations for spectroscopic investigations,<sup>[3-7]</sup> epimerisations,<sup>[8]</sup> double bond shifts,<sup>[9]</sup> b-eliminations,<sup>[9-12]</sup> and Li<sup>+</sup> complexation (alkyl-lithium activation)<sup>[13,14]</sup> have been reported. See Table 6 for a list of our P<sub>2</sub> bases with their properties, package size etc.

**Table 6. Phosphazene bases P<sub>4</sub>**Phosphazene base P<sub>4</sub>-t-Bu solution

1-tert-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ<sup>5</sup>,4λ<sup>5</sup>-catenadi(phosphazene)

pure, ~1.0 M in n-hexane C<sub>22</sub>H<sub>53</sub>N<sub>13</sub>P<sub>4</sub> Mr 633.7 [111324-04-0] 1 ml, 5 ml, 25 ml

Phosphazene base P<sub>4</sub>-t-Oct solution

1-tert-Octyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ<sup>5</sup>,4λ<sup>5</sup>-catenadi(phosphazene)

pure, 1.00 M ± 0.02 M in n-hexane C<sub>26</sub>H<sub>71</sub>N<sub>13</sub>P<sub>4</sub> Mr 689.8 [153136-05-1] 1 ml, 5 ml

**Applications:** These bases attract increasing interest in the field of anionic copolymerisation<sup>[13-18]</sup> and have also been utilized for solid-phase synthesis<sup>[9]</sup> related to combinatorial chemistry.<sup>[19,20]</sup> They have been reported to support alkylations,<sup>[1,21-31]</sup> Michael-additions,<sup>[15,32,33]</sup> aldol-reactions,<sup>[28,34-37]</sup> epoxide-opening,<sup>[17,19,38,39]</sup> acylations,<sup>[40]</sup> sulfonylations,<sup>[41]</sup> anionic oxy-Cope rearrangements,<sup>[42]</sup> oxidation of carbanions<sup>[37]</sup> and transition metal-induced coupling reactions.<sup>[29,43]</sup> Among the successfully converted low acidic substrates are alcohols<sup>[35,42]</sup>, amides<sup>[39,41]</sup>, peptides (N- and C-activation),<sup>[24]</sup> porphyrines,<sup>[4]</sup> phosphines,<sup>[28]</sup> H-phosphonates<sup>[31]</sup>, esters,<sup>[5,25,27,35]</sup> β-alkoxyesters<sup>[21]</sup> and -lactones<sup>[23,2118]</sup>, and β, γ, δ-lactones,<sup>[23,30]</sup> triesters,<sup>[40]</sup> sulfones,<sup>[3,34]</sup> episulfones,<sup>[28]</sup> benzothiazole,<sup>[21]</sup> and benzyl aryl ethers,<sup>[38]</sup> β-Hydroxy sulfones,<sup>[34]</sup> phosphonothioates,<sup>[31]</sup> enol triflates,<sup>[40]</sup> benzotranes,<sup>[36]</sup> and subphthalocyanines<sup>[44]</sup> are thus efficiently synthesized.

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